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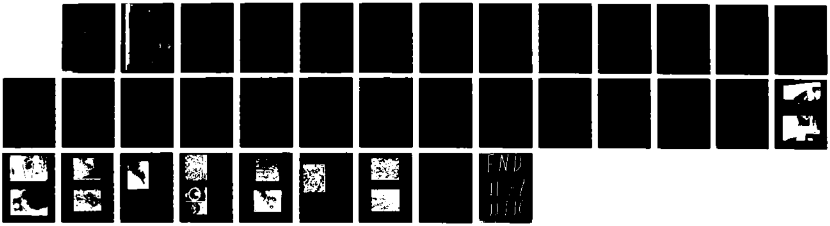

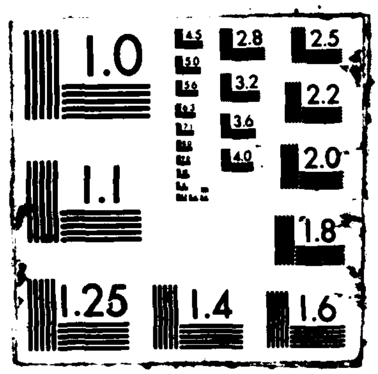
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DEPARTMENT OF DEFENCE

DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION

MATERIALS RESEARCH LABORATORIES

MELBOURNE, VICTORIA

REPORT

MRL-R-1060

AN EXAMINATION OF COATING FAILURE ON WING PIVOT FITTINGS OF F111 AIRCRAFT

L.V. Wake

Approved for Public Release

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ABSTRACT

Failure of replacement coatings on the wing pivot fittings in integral wing fuel tanks of F111 aircraft has resulted in serious corrosion and pitting on critical sections of the fittings. Failed paint flakes from the fittings were characterised by adhesive detachment of the epoxy polyamide priming coat. Examination of fuel and moisture resistance of a range of possible coatings has been undertaken against those currently in use. The results suggest that coatings based on epoxy polyamide resins are sensitive to glycol ether compounds employed as fuel system icing inhibitors in aviation turbine fuels. A more resistant epoxy polyurethane paint coating has therefore been proposed for use on the inspection areas of the fittings. It is also recommended that respraying over existing coatings inside the wing fuel tanks and on the fittings away from the inspection areas, a practice that has led to a series of intercoat adhesion failures following overhaul, be discontinued.

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AN EXAMINATION OF COATING FAILURE ON WING PIVOT FITTINGS OF F111 AIRCRAFT

L.V. Wake

1. INTRODUCTION

1.1 General Outline of Wing Pivot Fitting Coating Problem

The F111 wing pivot fittings (WPF's) form part of the wing integral fuel tanks and as such are immersed for lengthy periods in aviation turbine fuel and its additives. The fittings, being constructed of corrosion-prone D6AC steel, were originally protected by a coating scheme which comprised vapor deposited cadmium and a MIL-C-27725B fuel resistant polyurethane paint. This coating system was removed from certain areas of the fittings for nondestructive inspection prior to Cold Proof Load Testing (CPLT) in the early 1980's. The areas where removal occurred are the fuel flow holes ("mouse holes") along the central stiffener (Nos. 13-18) and adjacent to the wing pivot fitting hole (11,12,22,23) on the wing pivot lower plate and the corresponding vent holes along the central stiffener and the two adjacent stiffeners (Nos. 50-66) on the upper plate (Fig. 1). The coating was also removed from the five stiffener runouts on the upper and lower plates at this time (Fig. 1). In the intervening period since CPLT, the repaired areas have been restripped for examination during routine inspection. Failure of the replacement coatings has led to corrosion and pitting of the fittings in critical areas (Figs. 2 & 3). A serious cracking problem has also occurred on some of the reworked areas of the pivot fittings.

Two further types of coating failure have also occcurred after inspection and repair of wing pivot fittings. One of these has involved the adhesive failure of oversprayed paint which has detached from the original fuel resistant polyurethane coating (intercoat adhesion failure) in areas away from the repaired section (Figs. 4 & 5). The other has involved an isolated breakdown of the original vapour deposited cadmium on the fittings by its reaction with trace compounds in the Avtur fuel. This has resulted in the detachment of both the vapor deposited cadmium and overlying fuel resistant topcoat. (A similar failure has been observed in another area of the wing fuel tanks, described in Section 3.1).

History of Coating Repair Procedures

In 1967 (1), prior to RAAF obtaining the F111 aircraft, General Dynamics issued an Aircraft Engineering Instruction for 'Integral Fuel Tanks: the repair of'. This instruction recommended 'cadmium plated surfaces to be examined visually for damaged areas. Touch up where required shall be performed by brush cadmium plating as per PS 74 02-18 requirement'. Shortly thereafter, an instruction was issued (2) for the purpose of inspecting fuel flow/vent holes in the wing pivot fittings on all aircraft. The latter instruction recommended a different process involving the application of 'one coat of MIL-P-23377D epoxy primer followed by one coat of FMS-1046 (MIL-C-27725B equivalent) polyurethane fuel tank corrosion preventative coating in accordance with FPS-1004 for repair of reworked fuel flow holes'.

Pivot fittings on some RAAF F111 aircraft were repaired at CPLT by brush cadmium plating whereas others were repaired using the primer/topcoat paint scheme, a situation presumed by present Service personnel to have resulted from the two different instructions. Both systems were appplied in the US at McClellan Air Force Base, Sacramento (SM-ALC). The former system, viz, brush plated cadmium and fuel resistant polyurethane topcoat, was applied at RAAF's request although USAF was not employing this system on their own aircraft. This scheme was terminated on RAAF aircraft in 1982 following widespread corrosion problems, e.g. 'F111 A8-140 Sept. 82 - Attempts to isolate a fuel dumping problem necessitated removal of LH wing pylon drag link to enable the pivot fitting ducting to be inspected. This inspection revealed evidence of corrosion on numerous fuel flow and vent holes and stiffener runouts....The surface finish of fuel flow hole 50 was removed and it was found that the corrosion was in the interface of the CAD plating and the D6AC steel. Corrosion was evident on the following holes: 14,16,18,29,48,50, 51,58,59,60,61, and all stiffener runouts visible through the drag link access panel. The RH wing drag link was removed and the pivot fitting area inspected. Corrosion evidence was observed on holes 13,14,15,16,17,18,22, 23,49,50,51,52,53,54,57,58,59,60,61, and one upper and one lower stiffener runout. The same area on aircraft A8-139 was inspected and no evidence of corrosion was found. A8-139....has not had CAD plate applied during surface finish restoration' (3).

In September 1982, following 482 Squadron's Defect Report (3), STI F111C/345 (4) was issued replacing previous instructions (5,6) which required brush plating of the fittings by the adoption of the paint repair scheme. The instruction noted that 'until a thorough investigation of the problems is completed, this STI deletes all requirements to brush cadmium plate those D6AC steel components which are subsequently painted with epoxypolyamide primer'.

RAAF F111's in which pivot fittings were painted rather than cadmium plated at CPLT received the USAF paint repair scheme consisiting of an epoxy polyamide primer and a fuel resistant polyurethane topcoat. The epoxy primer used at SM-ALC, although clearly recognisable by composition, colour, etc. has not been sourced by Australian personnel. The topcoat used was Product Research Company's (PR 1560) revised epoxy polyurethane tank coating (MIL-C-27725B). This coating was used as topcoat for all repairs carried out between CPLT and August, 1986. This topcoat differs from the original fuel resistant epoxy polyurethane (PR 1563) present on the fittings at the time of aircraft delivery by containing chromium oxide as pigment whereas the original

coating contained strontium chromate and a filler whose elemental profile by energy dispersive X-ray analysis (EDXA) corresponds with asbestine. It is understood that manufacture of the original topcoat was terminated on environmental grounds. Where present on the pivot fittings, the original coating remains in excellent condition.

Since the epoxy polyamide primer/polyurethane paint scheme was adopted for all F111 aircraft in September 1982, a number of epoxy primers have been used on the wing pivot fittings. Some of these primers have met the MIL-P-23377D Specification whereas other have not. The first primer used, the unidentified apple green material applied at SM-ALC contains zinc chromate as inhibitor instead of the specified strontium chromate. The primer first applied in Australia to repaired areas of the fittings is understood to be a nonspecified grey green epoxy polyamide which also contained zinc chromate as inhibitor. This was replaced by Triton MIL-P-23377D primer, which met the Specification, and in turn by Anzol MIL-P-23377D primer in 1985. All of these primers have been involved in coating failures.

1.3 History of Coating Failure Corrosion

The history of painting defects on wing pivot fittings is not well documented. A number of RAAF Defect Reports since August 1985 detail the condition of the surface coating, however references appear in earlier Defect Reports noting poor surface condition or simply the presence of surface corrosion. Table 1 gives the reported condition of the pivot fittings in a number of aircraft. A close association between corrosion and crack formation is apparent from the records.

The first Defect Reports on coating failure on the pivot fittings, as mentioned, were the 1982 reports involving brush plated cadmium failure (3). These failures resulted in STI 354 (7) being raised in November 1982 to examine defects on wings which had been cadmium plated. RAAF records suggest that cadmium plating occurred on the pivot fittings of F111 aircraft Nos. A8-126, A8-134, A8-140, A8-146, A8-147 and A8-148 although other records suggest that A8-146 was not plated.

In September 1983, the first paint failure not involving brush plated cadmium was observed (8) on aircraft A8-145, RH wing (A-15-12). This failure resulted from the upper stiffener runouts and some fuel vent holes having been primed but not topcoated. Corrosion was present under the lifted paint on FVH's 13 and 14 (this wing had been painted at SM-ALC).

Failure of a complete paint scheme involving primer and topcoat was first observed (9) in December 1983 on both wings of aircraft A8-139. Cracking was also observed on No. 2 runout of the LH wing (A-15-39). As the wings had not been brush cadmium plated, the failure raised questions from SM-ALC on the implications for USAF.

By 1985, further failures of the paint on the repaired areas had been detected. These failures have become widespread and blistering/corrosion of the pivot fittings has now been observed on at least fourteen aircraft since that time (see Table 1).

1.4 RAAF Avtur Fuel Additives used at Amberley

A modification to RAAF procedures, which is considered to relate to this problem, is the change in composition of the aviation turbine fuel which occurred at Amberley in September, 1983. At that time the fuel system icing inhibitor (FSII), ethylene glycol monomethyl ether (EGME), was replaced by diethylene glycol monomethyl ether (DGME). Each of the FSII additives was employed in Avtur fuel at 0.15% v/v. It is understood that USAF continued to use EGME as FSII in the fuel for its F111 aircraft until recently.

1.5 Nondestructive Inspection Procedures for Wing Pivot Fittings

Following CPLT, non-destructive inspection has routinely been carried out on the fuel flow/vent holes and stiffener runouts to detect the presence of cracks in these highly stressed areas. The inspection procedure is presently undertaken with magnetic silicone rubber as the moulding compound (Dynamold MR 502, MR 502K or MR 502Y; Anglo-American Aviation Company) although cellulose acetate was formerly used.

The magnetic rubber inspection (MRI) process involves the use of electromagnets, a microscope and a Gauss meter during the application of a magnetic rubber base material/catalyst system to the inspection areas. Briefly, the process involves the curing of a plug of magnetic silicone elastomer on the metal surface in an electromagnetic field. The plug is then removed and examined for discontinuities which indicate the presence of cracks.

Correct practice during several steps in the magnetic rubber inspection process is considered crucial to paint adhesion on the repaired areas following inspection. The most critical of these is:-

(i) Effective removal of silicone contaminants prior to repainting. Also important are -

(ii) The complete removal of the Specification Lubricant (MIL-C-16173) applied to prevent corrosion of the stripped D6AC steel fittings during the inspection period; and

(iii) The "plasticine" used to form a dam around the curing silicone rubber mould.

2. EXPERIMENTAL

2.1 General

In this investigation, the paint coatings involved in the Service failures on the F111 pivot fittings were examined as follows:

(a) Failed samples of the coatings from the aircraft were examined for application problems and/or material deterioration.

(b) The coatings were applied to test coupons for laboratory trials.

The epoxy polyamide primers and polyurethane topcoats used on the pivot fittings are required to meet MIL-C-23377D and 27725B Specifications respectively. However, the above Specifications require all examinations to be carried out on aluminium whereas the field requirement under investigation is for coating and protection of high strength D6AC steel components. As such, the results from the Specification testing should be treated with caution. Further experiments on the coatings were therefore devised employing steel panels to overcome this problem (see Sections 2.3 and 2.4).

2.2 Failed Paint Samples from Service Aircraft

Fourteen samples of failed paint flakes from six aircraft were examined for possible causes of failure. Twelve of the samples were flakes which had detached from the F111 pivot fittings, one sample was obtained from a 'wing carry-thru box' failure and another from a failure in an aft fuel tank. Three samples of intact paint were scraped off the wing pivot fittings for comparison.

2.3 Examination of Paint Flakes from Service Aircraft

Flakes from each failure sample were examined by light microscopy and scanning electron microscopy (SEM)/Energy Dispersive X-ray Analysis (EDXA). EDXA was also used to identify contaminants under the primers.

The basecoat surface of two failed flakes (ex sample 13) was examined by electron scanning for chemical analysis (ESCA). The same flakes analysed by ESCA were also examined by infrared (IR) spectroscopy and compared with cleaned coatings.

2.4 Laboratory Immersion of Painted Coupons

Two series of immersion trials were carried out to determine the fuel resistance of candidate coatings applied to steel panels. In the former trial four primers and two topcoats were evaluated on coupons in a number of fuel mixtures for evaluation. The coatings are shown in Experimental Section 2.5.

The panels for the first trial were painted as follows: two-thirds of the panel was painted with primer and two-thirds of the panel painted with topcoat. The topcoat was applied from the opposite end of the panel to the primer resulting in three paint zones, a zone at each end of the panel being coated with either primer or topcoat and a central zone being coated with primer and topcoat. After curing for 10 days, panels from each series were weighed and immersed into one of five fuel mixtures. The Avtur fuel mixtures employed included two containing diethylene glycol monomethyl ether (DGME) as FSII, another with ethylene glycol monomethyl ether (EGME) as FSII, a fourth with 2-methyl-2,4 pentanediol (hexylene glycol) as FSII and a fifth with no FSII additive. The fuel mixtures contained HiTech 515 (30 ppm), the corrosion inhibitor/lubricity additive employed in Australia, except one of the DGME mixtures which had HiTech 580, one of the additives used overseas, at the same concentration. The panels were immersed in the fuel mixtures for 12 weeks, removing and reweighing the panels at intervals of three weeks. A small water droplet was placed in contact with each zone of the coating. (The high solubility of the FSII in water results in the glycol ether partitioning preferentially into that phase. The resulting water/FSII droplet provided information on relative coating resistance). At the end of the immersion period, the panels were removed and "wet" adhesion measurements carried out within an hour of removal (see Section 2.5 below). Primers which had formed small blisters under the water/FSII droplets were stripped and examined for corrosion.

Three primers and one topcoat were employed for the second immersion trial. The coatings were: primers (i), (ii) and (iii); topcoat (vi) below (Section 2.6). Each of the four coatings was separately applied to a number of coupons and cured for 10 days. In this trial the number of Avtur fuel mixtures was increased. In addition to the use of DGME and EGME, Avtur fuel mixtures containing (a) ethylene glycol (b) diethylene glycol (c) propylene glycol monomethyl ether (PEGME) and (d) dipropylene glycol monomethyl ether (DPGME) were investigated for their effect on coatings. HiTech 515 (30 ppm) was added to the additional fuel systems. This trial was undertaken with the aim of determining solvent factors affecting coating behaviour and possible FSII replacements for DGME.

Two further panels were treated with Dow Corning - glycidoxytripropylmethoxysilane adhesion promoting agent (Z-6040) at 1.5% in an acetone/H_2O:4/1 mixture. The panels were immersed in the solution for 30 minutes and then dried in an oven at 80°C for 60 minutes. On cooling, both panels were painted with Deft primer, one being immersed in the EGME/Avtur fuel system and the other in the DGME/Avtur fuel system.

2.5 "Wet" Adhesion Tests following Laboratory Immersion

The adhesion test, described below, was devised during this investigation in an attempt to measure the relative adhesion values of the different coatings on steel panels following extended periods of immersion in the various fuel mixtures. This determination is referred to herein as the "wet adhesion test".

The adhesion values were determined by an Epprecht Twistometer measuring the torsional force applied to a "dolly" which was adhered to the paint film using 'Repco Super-Glue-3'. The hexagonal "dollies" were bonded to the test surface by applying a continuous film of the 'Super Glue' immediately after excess fuel mixture had been wiped from the paint surface. The test panels were allowed to cure for 50 minutes and the adhesion value measured. The force used to remove a unit area of the paint film could therefore be determined.

(Evaluation of the adhesion values of the 'Repco Super Glue' with increasing time on the panels showed that the bond strength had attained approximately 95% of its final strength after 15 minutes and increased slowly thereafter. The adhesion strength of the coatings also increased with time after removal from the Avtur fuel mixtures. It was decided that the time of 50 minutes was optimal for adhesive cure/primer dryout. It was also felt that this period of 'drying time' might approximate that occurring to the coating on the pivot fittings during operational flying conditions.

2.6 Paints for Investigation

(a) Primers

(i) 'Anzol Yellow MIL-P-23377D epoxy polyamide primer' (Manuf. No. D685-9002 (curing agent)/691-3005 (base)).

(ii) 'Deft MIL-P-23377D epoxy polyamide primer' (Manuf. Ref. No. 02-4-24 (curing agent)/02-4-24)).

(iii) Anzol Super Koropon Fluid Resistant' epoxy polyamine primer (Manuf. Ref. No. D676-9001 (curing agent)/D666-2001 (base)).

(iv) 'Triton Aircraft Grey-green' epoxy polyamide primer (Manuf. Ref. No. 0431-8100 (curing agent)/0430-3784 (base)).

(b) Topcoats

(v) Products Research Company PR-1560-M (Manuf. Ref. No. C-32785 (pts A & B)).

(vi) 'DeSoto Integral Fuel Tank Coating' (Manuf. Ref. No. 910-702 (curing agent)/823-707 (base)).

2.7 Miscellaneous Examinations

The primers and topcoat (v) were applied to colour cards to examine the spray characteristics and covering power of the various coatings. Droplets of water/DGME were added to small areas of the coatings to examine the effect of such mixtures. The fluid inside the blisters which formed overnight was examined by gas chromatography/mass spectrometry.

3. RESULTS

3.1 Examination of Paint Failures from Service Aircraft

Examination of failed paint flakes from the inspection areas of a number of pivot fittings showed that failures had resulted from adhesive detachment of epoxy polyamide primers from the substrate. The lower surface of the primers involved in these failures was characterised by breakdown of the binder matrix. This breakdown appeared to have been accelerated where contaminant inclusions were present under the primer (Figs. 6 and 7). A number of different contaminants were observed under failed paint including - silicone rubber residues, organic fibres, chrysotile asbestos, calcium carbonate deposits, unidentified organic residues and pigment aggregations.

Other adhesive failures were observed which had occurred as a result of paint application problems. These include excessively thick coatings of up to 700 um thickness.

A further problem causing coating failure on the pivot fittings was breakdown of the original vapor deposited cadmium. This failure occurred on one of the upper stiffeners on aircraft A8-114. The cadmium had reacted with a sulphur material, presumably the sulphur present in Brisbane fuel, and the product had detached removing the overlying original PR1563 polyurethane paint with it. The cadmium/sulphur reaction product was relatively thick along one edge of the failure (Fig. 8). (A similar failure occurred under paint and sealant in a wing tank as a result of breakdown of the vapour deposited cadmium. In this case the reaction product was a cadmium/phosphorus compound (Fig. 9)).

Following priming of the inspection areas, it is apparent that these and all other surfaces inside the wing tanks, the wing carry-thru box and other fuel tanks were resprayed with the replacement topcoat to provide a uniform coating appearance. This practice has been confirmed by the relevant Service personnel. Widespread adhesive paint failures have occurred with this repair scheme, resulting in detachment of the oversprayed polyurethane topcoat from the original fuel resistant topcoat away from the inspection areas of the pivot fittings (Figs. 4 and 5). The condition of the failed topcoat from the blistered areas shows evidence of binder breakdown (Figs. 10 and 11).

3.2 Chemical Analysis of Failed Paint

Investigation of the detached surface of the unidentified apple green primer by FT-IR inspection has tentatively identified a carboxylate salt on the lower surface of the failed epoxy polyamide primer. Examination by ESCA showed a high level of sodium content on thos lower surface.

3.3 Results of Immersion and "Wet" Adhesion of Coatings in Avtur Fuel Mixtures

3.3.1 Immersion Trial 1

The results of the immersion tests are shown in Tables 2 to 5. The primers showed a general decrease in adhesion strength of approximately 40% on immersion in straight Avtur (i.e. without FSII) compared to that of the corresponding unimmersed panels. The addition of an FSII additive further reduced the adhesion of some primers, notably the Deft coating formerly used by USAF, and the Anzol Yellow coating recently used by RAAF. Of the various icing inhibitors, DGME had the greatest effect on primers, reducing adhesion levels of the DEFT and Anzol coatings to 60% of the levels in straight Avtur (ca. 35% of dry adhesion levels). The Triton grey-green primer, a harder and more brittle coating was less effected than the other two epoxy polyamide primers. Super Koropon primer, based on an epoxy aminosilane adduct, was more resistant than the other primers.

The changes in adhesion level of the primers in Avtur show an approximate correlation with the appearance of blisters under the FSII/water droplets, i.e. primers with low "wet" adhesion levels tended to blister readily under the water/FSII droplets. The adhesion levels also show a relationship with the weight changes of the coating systems, higher weight increases (i.e. greater swelling) correlating with lower adhesion levels. Replacement of HiTech 515 by 580 in DGME showed no consistent effect on the coatings.

The MIL-C-27725B polyurethane coatings were found to be unaffected by the various Avtur fuel mixtures. (Only DeSoto Integral Fuel Coating passed the MIL-C-27725B Specification).

3.3.2 Immersion Trial 2

A similar pattern of coating/fuel interactions occurred in this trial as in Immersion Trial 1. In addition, the two propylene based glycol ethers included in this trial, namely PGME and DPGME, were found to have less effect on coating weight increase i.e. swelling, than DGME/Avtur mixtures. The swelling effects were similar to those caused by EGME/Avtur mixtures.

The two glycol compounds included in this trial, viz. ethylene glycol and diethylene glycol caused greater swelling of the coatings than did any of the glycol ethers. The weight increases of the coatings in diethylene glycol are larger than the former and continue to rise steadily (after 5 months) whereas the others have levelled out.

The silane treated panel immersed in DGME/Avtur showed lower weight increases on immersion than the corresponding untreated panel. The silane treated panel immersed in EGME/Avtur showed no difference to that of the untreated panel immersed in the same solution.

3.3.3 Miscellaneous Examinations

As indicated in the Experimental Section, blisters formed under the coatings which had been sprayed on the colour cards. The results of the GC/MS analysis showed the presence of DGME.

The results of the salt spray examination (Table 6) suggest that the Super Koropon is a more resistant primer than the corresponding epoxy polyamide primers. The DeSoto Integral Fuel Tank Coating showed the best resistance to salt spray exposure of all coatings examined.

4. DISCUSSION

4.1 Coating Failures Resulting from Application Problems

Repainting of the pivot fittings on the F111 at overhaul has been a time consuming and difficult problem for RAAF personnel since routine inspections were undertaken. The process is made difficult by the fact that the operation is carried out through access holes to the wing fuel tanks small enough to preclude painters from seeing into the tank while respraying the inspection areas. In fact, some of the larger painters employed at Amberley cannot fully insert their arm through the access holes. The procedure is further complicated by the requirement for the front, top and rear surfaces of the stiffener ribs to be repainted. As the view of the rear surfaces of the ribs is obscured from the access holes, mirrors and torches are required to inspect these areas following repainting. The pivot fittings at the top of the tank are more difficult to repaint than those at the bottom, especially those immediately inside the access holes when the wing cannot be inverted (e.g. R3 inspection). Earlier repaints in Australia were performed with a paint brush, however respraying is now carried out with a small air brush. Having recently become aware of the critical importance of the coatings on the pivot fittings, painters are now taking greater care with these areas. Paint stripping, crack inspection and cleaning, which are also hampered by the difficulties of access described above, are likewise receiving greater attention.

In view of the application difficulties confronting operators, some variation in paint thickness is understandable. However, the excessively thick (700 um) sections of some detached paint flakes were found to fracture under slight bending and failed the MIL-C-23377 and MIL-C-27725 flexibility tests. These thicker sections applied in former times have insufficient flexibility for use on the fittings which experience considerable flexing during flying.

4.2 Coating Breakdown on Inspection Areas of the Pivot Fittings

4.2.1 Organic Coatings

The evidence available from the results of the immersion trials and Service failures suggests that the problem of degradation of the primers on the pivot fittings, a problem aggravated by surface contamination, appears to involve solvent/resin interaction. Additional observations made during the investigation which are considered relevant to this interaction include:

(i) Glycol ether/water droplets readily softened the primers (the partition of the glycol ether between water and fuel is such that the glycol ether concentration may be as high as 45% v/v in these droplets).

(ii) Coatings applied to porous substrates were observed to blister overnight under droplets of water/DGME in Avtur. Gas chromatography-mass spectrometry of the fluid in these blisters showed that the DGME was present in the blisters under the coating.

(iii) The most severe breakdown of the coatings on the aircraft occurred around foreign inclusions, particularly around porous contaminant particles.

Further information on the coating breakdown process is derived from microscopic examination of Service failures. Deposits of a chromium compound were found on a number of the failed primer paint flakes. The morphology of some of these deposits is difficult to explain other than by precipitation from aqueous solution (Figs. 12a and b). The various chromium deposits show a similarity in composition although the form of chromium has not been determined (a corresponding cation concentration, as present in the coating, is not apparent in the EDXA profiles - see Fig. 12).

The degree of breakdown of failed coatings obtained from the tanks and pivot fittings was generally not observed on laboratory immersed coatings after 12 weeks. However, at the end of the immersion period, the area of the coatings directly under the water /FSII droplets on the epoxy polyamide primers showed a degree of etching approaching that of the field samples. The etching is presumed to be the result of physical swelling and/or chemical attack of the coating. The similarity in appearance of the coatings from (a) Service failure and (b) immersion trial are shown in Figs. 13 and 14.

IR analysis and ESCA investigation of the failed surfaces of the epoxy primers tentatively suggest that hydrolysis of groups (fatty acid moieties) present in these coatings has occurred. Differentiation between physical swelling of the coating and the onset of chemical attack would require further examination by microscopic IR in association with EPMA.

The silane-based adhesion promoters improved the performance of the epoxy polyamide primer in Avtur/DGME. The improved performance was less than the fuel resistant coatings, i.e. the epoxy polyurethane and the epoxy aminosilane. In view of the ester linkages in the coating on the treated panel, this result is not surprising.

A number of overseas researchers have made observations pertinent to the present coating failures. Hammond et al (10) observed saponification and adhesion loss of an epoxy ester primer from a bare steel substrate. Perhaps more relevant to the present circumstances is the recently demonstrated ability of some glycol ether compounds to chemically attack paint resins (11). Details of the mechanism of this attack are not known at this time, however the system involves an alkyd resin containing labile fatty acid moieties similar to those present in the epoxy primers. Rapid hydrolysis of ester groups in polyurethanes has also been observed in other organic solvents (12).

The ability of the glycol ethers to disrupt coatings was encountered elsewhere during this investigation. FSII concentrates removed the coating from their steel containers at the Brisbane terminal which had been painted with high solids epoxy coatings. The operators (Caltex Aust.) have replaced these storages with stainless steel tanks. The onset of the paint failures in September 1983 coincided with the change of FSII additive. The ability of the glycol ether compounds to act as paint strippers for epoxies and urethanes was noted elsewhere in 1985 (13).

Conditions for resin/fuel reaction are increased in RAAF F111's compared to USAF aircraft by the immersion of the pivot fittings in the Avtur fuel mixture for lengthy periods at Amberley. The procedure for local aircraft is to refuel following flying operations and then remain at the squadron 'taxiport' until required. Commonly, this may be of the order of 3-4 days although periods of a few weeks or a month are not uncommon. In contrast, USAF aircraft tanks are not refuelled during periods of aircraft storage (14).

4.2.2 Vapour Deposited Cadmium

Breakdown of the vapour deposited cadmium on the stiffeners was a small and isolated failure. The cadmium reaction products on the failed coating were thicker on one side of the blister and gradually diminished across the failed area. It is believed that this failure occurred adjacent to a blistered rework area of the fitting exposing the edge of the cadmium to the fuel. The failure of the vapour deposited cadmium that occurred elsewhere in the wing fuel tank is more complex as these areas are frequently scratched by the dental picks and probes used to remove sealant during the deseal/reseal process. Whatever the mechanism of the failure, it is apparent that the cadmium has been exposed to HiTech 515. The characteristic morphology of the cadmium/phosphorus complexes resulting from the reaaction of the phosphorus material in HiTech 515 with cadmium had earlier been observed on components in aircraft fuel systems by Sanders et al (15).

4.3 Coating Breakdown on Non-inspection Areas of the Pivot Fittings

The polyurethane topcoat oversprayed on the existing fuel resistant polyurethane away from the inspection areas of the pivot fittings is detaching over wide areas. While widespread, it is not considered to be a serious coating problem, (although it may cause a fuel supply line problem) as the original fuel resistant coating under the overspray remains in excellent

condition. As such, USAF do not repaint these areas resulting in a nonuniform appearance around the rework areas. It is understood that this procedure operates satisfactorily. (RAAF intend to adopt USAF practice and leave the noninspection areas untouched).

Loss of integrity of the detached polyurethane coating could be seen under the microscope (Fig. 10). This breakdown was surprising in view of the fact that the original polyurethane, where present in the tanks, remained in excellent condition. The replacement coating is now known to be based on a polyester rather than a polyether resin, and is believed to be undergoing hydrolysis of the ester groups. (The manufacturer has since recommended against this material being used in fuel tanks).

4.4 Laboratory Investigation

From the immersion trials, it is evident that diethylene glycol has a greater effect on the coatings than the other glycol or glycol ethers. Of the glycol ethers, DGME caused greater swelling than the other ehters examined. The minor effects on the coatings caused by PGME and DPGME are encouraging as these compounds, with their greatly reduced toxicity, are considered to be potential FSII additives.

4.5 Solubility Parameters

In recent times, the use of solubility parameters has provided a simple method of predicting the mixing ability (solubility, compatibility, etc.) of organic compounds. Partial solubility parameters, termed Hansen parameters, which measure the dispersion, polar and hydrogen bonding forces (d_d, d_p, d_h), are the parameters most commonly employed for prediction of the behaviour of paints and solvents. The magnitude of the effects of the glycols and glycol ethers on the coatings was surprising at the concentrations present in Avtur solution (0.15% v/v). Calculations based on the Hansen values of the additives in mixed solutions suggest that negligible effects would be expected at this level. An explanation for the considerable effect of the FSII additives is possibly based on the fact that the low solubility of DGME in Avtur reflects the weak interactions between this glycol ether and the kerosene. In such cases, strong positive deviations from Raoult's Law[1] are known to occur resulting in partitioning preferentially to the site of a stronger interaction. In addition, solubility parameter theory does not behave very well for these hydrogen bonding compounds capable of multiple specific interactions.

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1 Raoult's Law states that in an ideal mixture, the partial pressure, i_p, of any component i is given by the product of the mole fraction, i_x of component i and the saturation pressure i_{ps} of component i.

5. USAF F111 PAINT FAILURE/CORROSION PROBLEMS

Reports of corrosion on USAF F111 wing pivot fittings have occassionally appeared in the 'Corrosion Summaries' published regularly by the US Department of the Air Force, e.g. March 1986 (16) *"F111 Wing Pivot Fitting Stiffener Runout and Fuel 'Mouse Holes'*. The F111 wing pivot fitting stiffener runouts and fuel 'mouse holes' are being found corroded during PDM inspections. SM-ALC/MMKRC is working on this problem". Australian Service personnel involved with the problem believe that the problem in the US appears to be less severe and the occurrence less frequent than in Australia.

During a visit by RAAF personnel (AIRENG1), photographs were obtained of corrosion and cracking which occurred in the fuel vent hole 13 on a USAF F111. From the cast taken of the reworked hole, "blending of the crack removed about 5/16 inch of material. This is the largest FVH 13 crack discovered by SM-ALC and has given ASIP engineers cause to reflect on the longevity of the WPF if no re-inforcement is fitted....During discussions, SM-ALC engineers revealed that corrosion had been recently found in a number of previously re-worked WPF runouts and holes (17)".

The failure of the coating and the subsequent corrosion experienced by RAAF and USAF aircraft raises a number of questions on the relative severity of the problem. There appear to be five major differences in operation and maintenance of the RAAF and USAF F111 aircraft. These are:

(i) Different FSII additives.
(ii) Different lubricity additives.
(iii) Different primers.
(iv) Different stripping, cleaning and repainting practices.
(v) Different fuel storage practices.

From this study there appears to be clear evidence for the influence of FSII additives on particular coatings. No conclusive differences were seen between the lubricity additives on the coatings examined. The comparative performance of the primers recently used by USAF and RAAF were not markedly different. Of the maintenance procedures adopted in the US and Australia, similar care appears to be given to the stripping, cleaning and repainting practices, according to the relevant Service personnel. Finally, it is believed that the different fuel storage practices in the two countries may be important.

6. CONCLUSIONS

1. Epoxy polyamide coatings with ester linkages are sensitive to the glycol ether additives in Avtur. Glycol ether/water droplets considerably softened the primer coatings. There is evidence of chemical attack on the coatings.

2. The polyurethane coating used as topcoat in the interval between CPLT and 1986 also suffered loss of integrity in Service. This coating is likewise known to have polyester linkages. A replacement polyurethane coating has shown improved resistance in the laboratory immersion trials.

3. The propylene based glycol ethers had less effect on coating swelling and adhesion than corresponding levels of DGME.

4. The failure of a small area of vapor deposited cadmium is believed to have occurred when an adjacent paint failure exposed the metallic coating to Avtur additives.

7. RECOMMENDATIONS

1. The results of the immersion tests suggest that the chromated epoxy polyurethane, DeSoto Integral Fuel Tank Coating, be used to protect the repair areas of the wing pivot fittings.

2. Respraying of areas of the integral wing fuel tanks away from the repair areas of the fittings has resulted in adhesive paint failure and should be discontinued.

3. The propylene based glycol ethers should be examined for suitability as future FSII replacements for DGME in view of their minor effect on the fuel tank coatings.

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TABLE 1

Defects of F111 Wing Pivot Fittings

Aircraft Numbers	Wing Serial Numbers	Paint Condition and Corrosion	Defect
109	A15-82 (RH)	Blistering	Pitting
	A15-83 (LH)	Blistering	Crack
112	A15-121 (LH)	Not known	Nil defects
	A15-122 (RH)	Not known	Nil defects
114	A15-295 (LH)	Corrosion	Pitting
	A15-296 (RH)	Corrosion	2 Cracks from corrosion
126	A15-42 (RH)	Blistered	OK
	A15-41 (LH)	Blistered	Pitting
127	A15-3 (LH)	Corrosion	Pitting
	A15-4 (RH)	Corrosion	Crack
131	A15-22 (RH)	Corrosion	Minor pitting
	A15-21 (LH)	Corrosion	Minor pitting
132	A15-15 (LH)	Corrosion	Pitting
	A15-16 (RH)	Corrosion	Cracks
135	A11-16 (RH)	Corrosion	Cracks
	A11-15 (LH)	Corrosion	Pitting
139	A15-37 (LH)	Not known	Cracks
	A15-38 (RH)	Not known	Pitting
140	A15-47 (LH)	Corrosion	Pitting
	A15-48 (RH)	Corrosion	Cracks
144	A15-8 (RH)	Corrosion	Crack
	A15-7 (LH)	Blistering	OK
144	A15-39 (LH)	Blistering	Not known
	A15-40 (RH)	Blistering	Cracks
145	A15-46 (RH)	Blistering	Cracks
	A15-45 (LH)	Blistering	Cracks
146	A15-44 (RH)	Blistering	Not known
	A15-43 (LH)	Not known	Not known
147	A15-12 (RH)	Not known	Not known
	A15-11 (LH)	Not known	Not known
42	A15-36 (RH)	Corrosion	Minor pitting
	A15-35 (LH)	Corrosion	Minor pitting
43	BA15-3 (LH)	Corrosion	Minor pitting
	BA15-4 (RH)	Corrosion	Minor pitting

TABLE 2

Wet Adhesion of Epoxy Primers (kgf/cm^2)#

Avtur Additive	Primer/Topcoat			
	Deft/ PRC	Anzol Yellow/PRC	Triton Grey-Green/PRC	Anzol+ S-Koropon/PRC
DGME + E580	102	125	195	>200
DGME + E515	100	135	198	>180
EGME + E515	180	175	>180	>190
Hexylene Glycol + E515	160	172	195	>180
E515	190	190	210	200*
Dry Panel**	325*	330*	340*	345*

+ Silane Adducted Coating
* Cohesive failure
** Adhesion of unexposed paints determined after 24 hours curing of super strength Araldite

TABLE 3

Weight Increase of Coating after Immersion

Avtur Additive	Primer /Topcoat			
	Deft/ PRC	Anzol Yellow/PRC	Triton G-green/PRC	Anzol S-Koropon/PRC
DGME + E580	2.2%	2.7%	1.45%	1.35%
DGME + E515	2.1%	2.5%	1.8%	1.6%
EGME + E515	1.1%	1.3%	1.2%	0.3%
Hexylene Glycol + E515	1.7%	1.5%	1.3%	0.3%
E515	0.8%	0.45%	0.45%	0.3%

TABLE 4

Effect of Water/FSII on Epoxy Primers

Avtur Additive	Primer			
	Deft	Anzol Yellow	Triton Grey-Green	Anzol Super-K'pon
DGME + E515	B(D)	B(D)	SB	SB
DGME + E580	B(D)	B(D)	VSB	SB
EGME + 515	SB	B	G	G
Hexylene glycol + E515	D	B	G	G
E515	D	B	G	G

D = Discolored
B = Blisters
VSB = Very small blisters
G = Good

TABLE 5

Weight Increase of Coating after Immersion

Avtur Additive	Primer			Topcoat
	Deft	Anzol Yellow	Super Koropon	DeSoto Int. FTC
Ethylene Glycol (EG)	3.5%	3.1%	1.3%	0.25%
Diethylene Glycol (DiEG)	5.29%	5.07%	1.4%	ND
EGME	0.8%	0.9%	0.37%	0.01%
DGME	1.41%* 2.02%	1.70%	0.6%	0.2%
PGME	0.49%	0.74%	0.3%	0.0%
DPGME	0.92%	0.74%	0.2%	0.0%
Control	0.47%	0.65%	0.1%	0.0%

ND = Not determined
* = Silane treated panel

TABLE 6

Salt Spray Examination on Steel

Coating	Time to Failure (hrs)
Anzol Yellow	144
Triton Grey-green	168
Super Koropon*	312
DeSoto Int. FT Coating	>500

* Coating half thickness (10 uM)

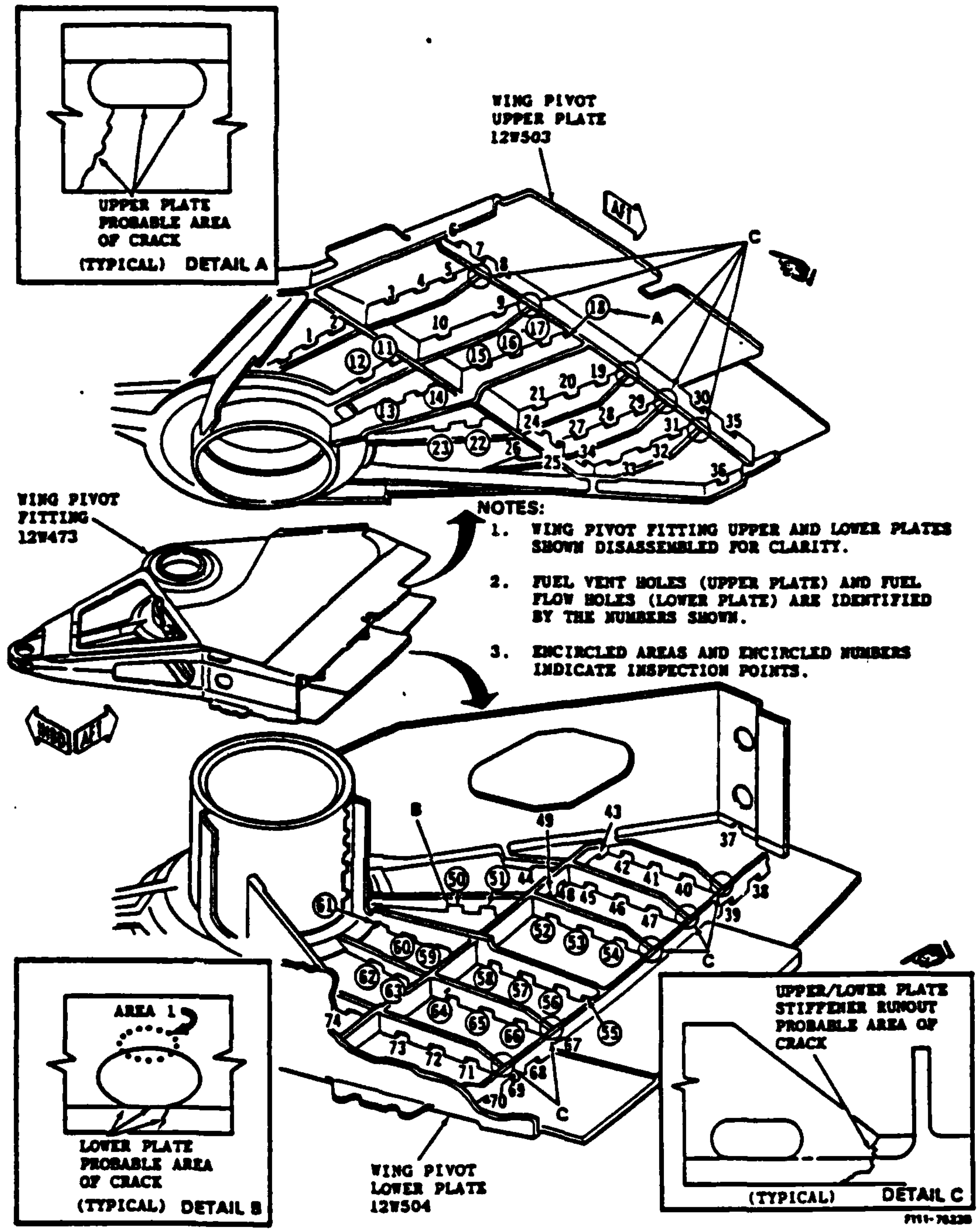

Fig. 1. Wing Pivot Fitting - Fuel Flow/Vent Holes and Stiffener Runouts

Fig 2. Epoxy polyamide primer and polyurethane topcoat on the pivot fittings inside the wing fuel tanks prior to paint removal for inspection. Aircraft A8-140.

Fig 3. Wing pivot fittings after paint removal. Corrosion is apparent around the fuel flow holes. Aircraft A8-140.

Fig 4. Failure of the oversprayed polyurethane topcoat inside the wing fuel tank. The original fuel resistant is apparent under the detached area of paint. Aircraft A8-140.

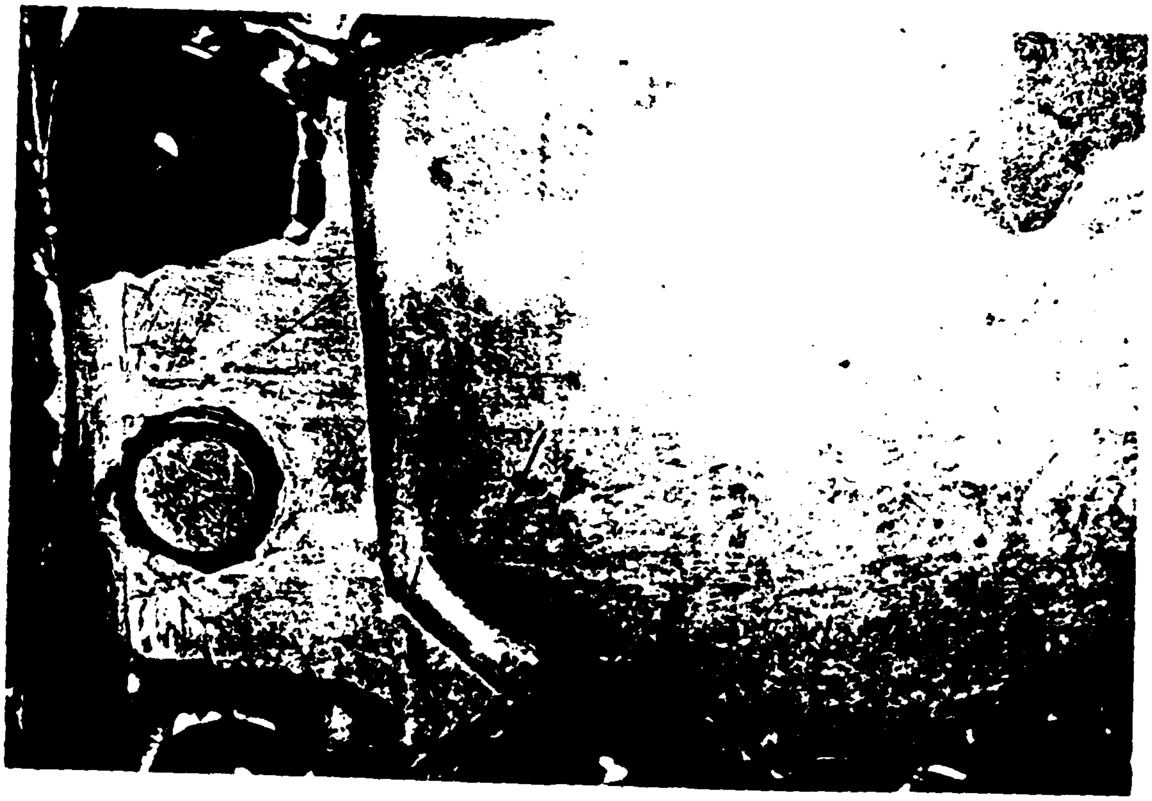

Fig. 5 Failed and detached oversprayed polyurethane inside the wing fuel tank. Some loss of sealant is apparent. Aircraft A8-140.

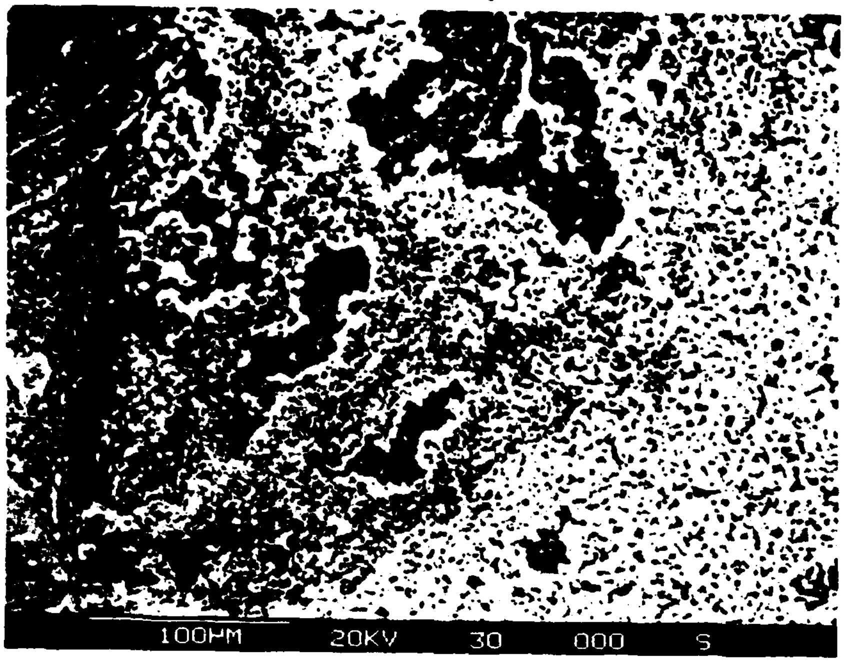

FIG. 6 Severe failure of unidentified primer around a silicone rubber inclusion. Paint from Aircraft A8-114 wing pivot fitting. Lower surface of paint flake.

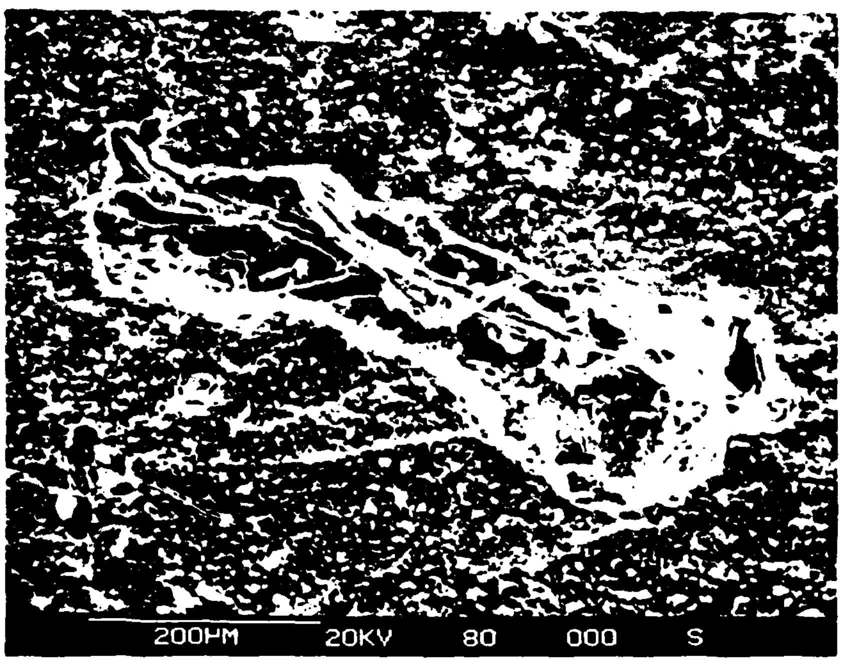

FIG. 7 Paint failure of PR 1560 topcoat around an organic fibre inclusion. Aircraft A8-135 aft fuel tank. Lower surface of paint.

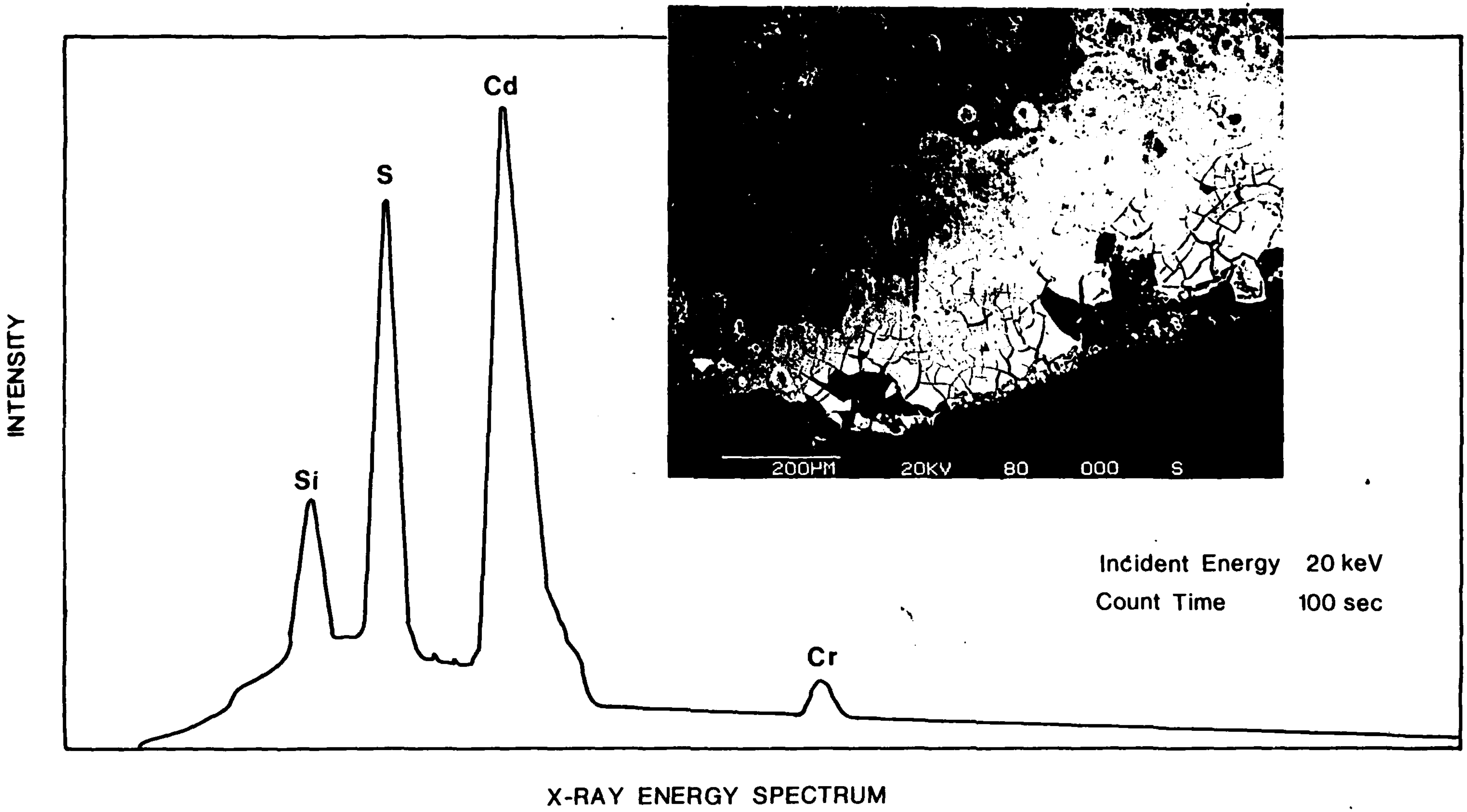

Fig 8. Cadmium/sulphur reaction product. The thickness of the product is much heavier adjacent to one side of failed paint flake. (Silicone peak from filler in coating). Aircraft A8-140.

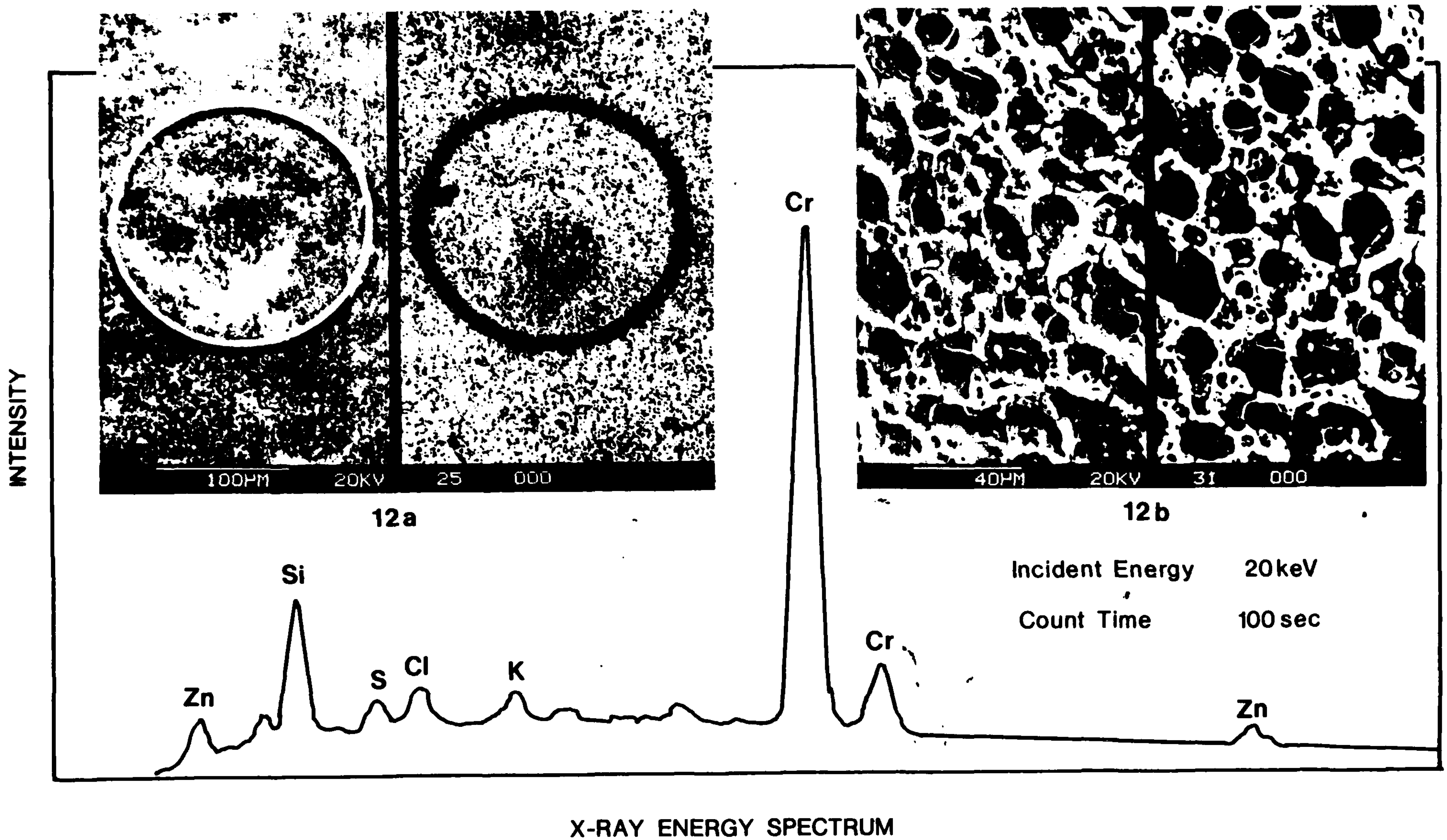

Fig 9. Cadmium/phosphorus reactive product. The cadmium had failed under the replacement polyurethane topcoat and sealant. Wing carry-thru box. Aircraft A8-145. Replacement paint and sealant failed after several days curing before fuel had been reintroduced.

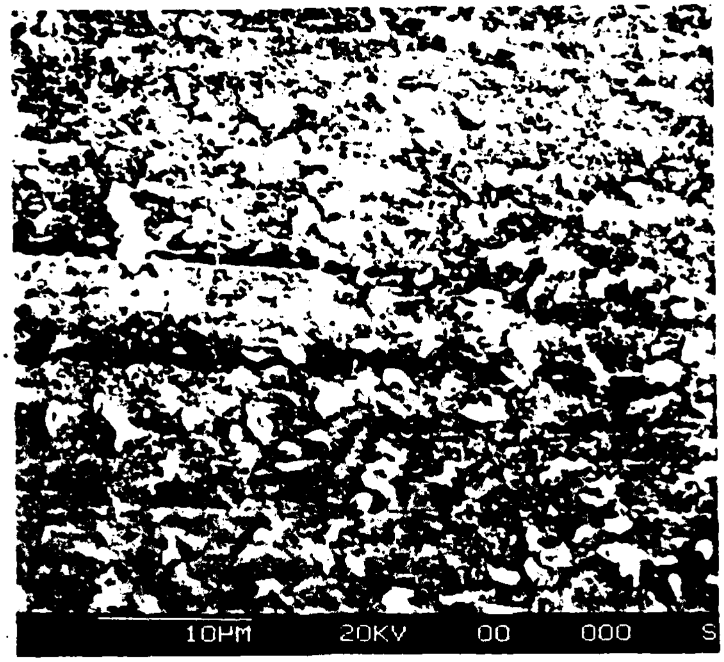

FIG. 10 Early stages of paint failure. Etching of binder leaves pigments proud of surface (PR 1560 topcoat). Paint from Aircraft A8-114, wing pivot fitting. Lower surface of detached paint flake.

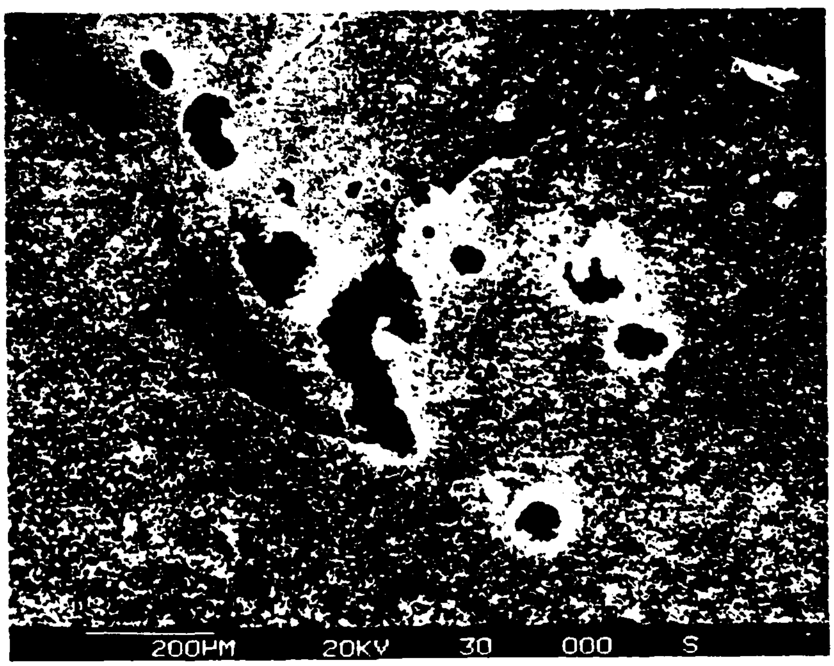

FIG. 11 Advanced paint failure of PR 1563 topcoat. Paint from Aircraft A8-140. Lower surface of paint flake.

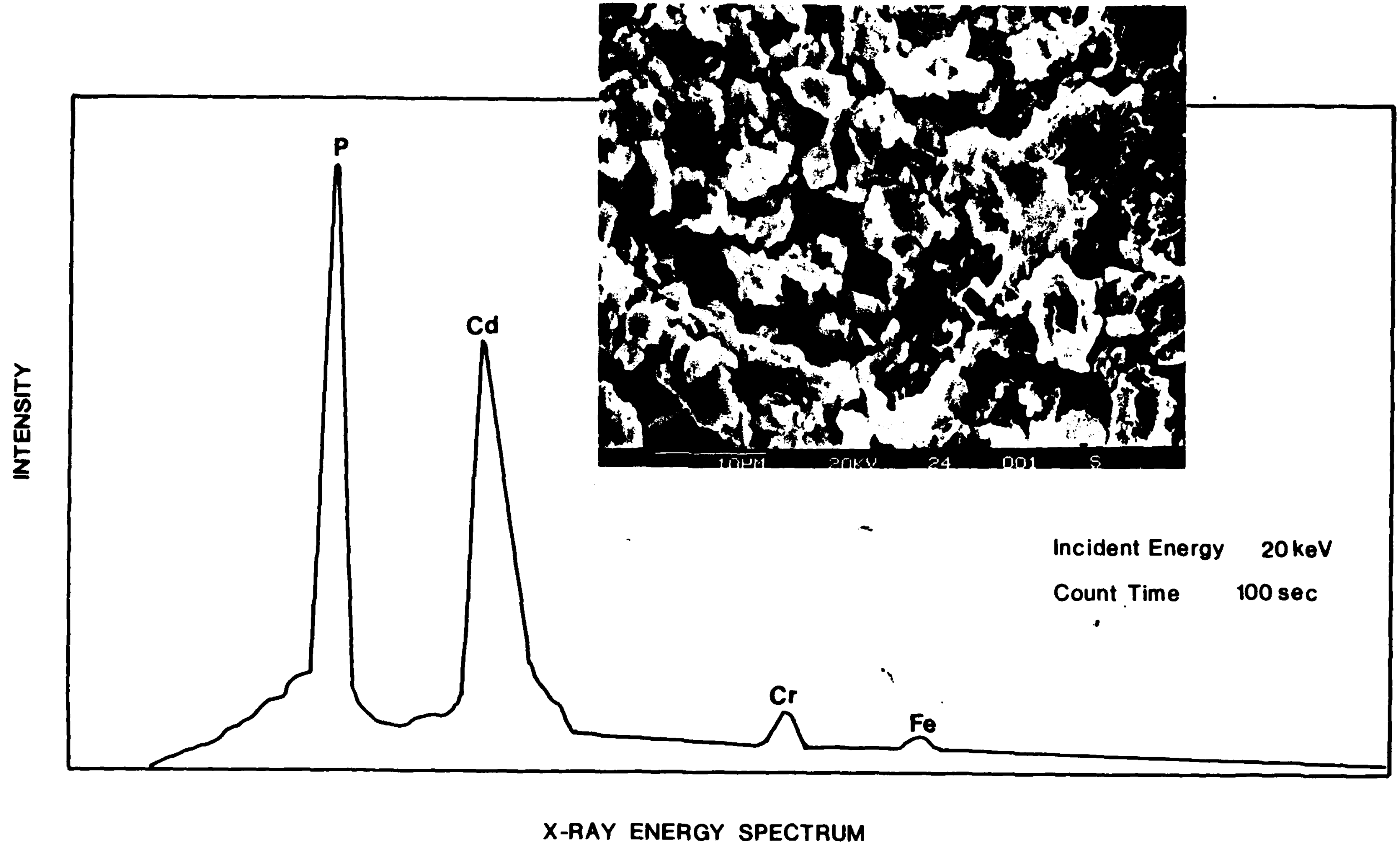

Fig. 12. EDXA spectrum of annular chromium deposit shown in Fig. 12a. The chromium deposits shown in both figures were present on top of failed primer flakes. Paint flakes from aircraft A8-148 wing pivot fitting. Flakes composed of 'US' primer and grey-green primer.

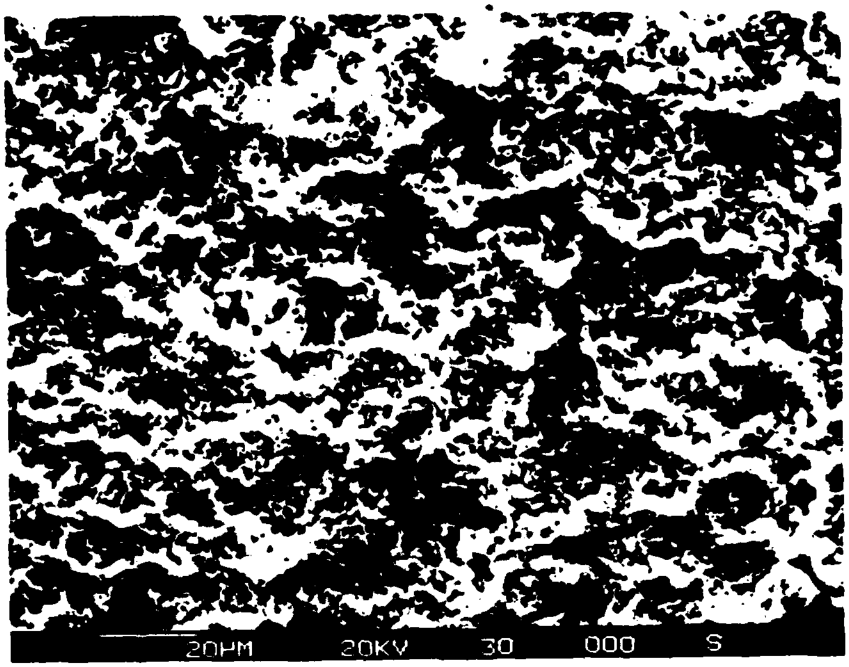

FIG. 13 Paint failure from Aircraft A8-135 showing loss of binder from coating.

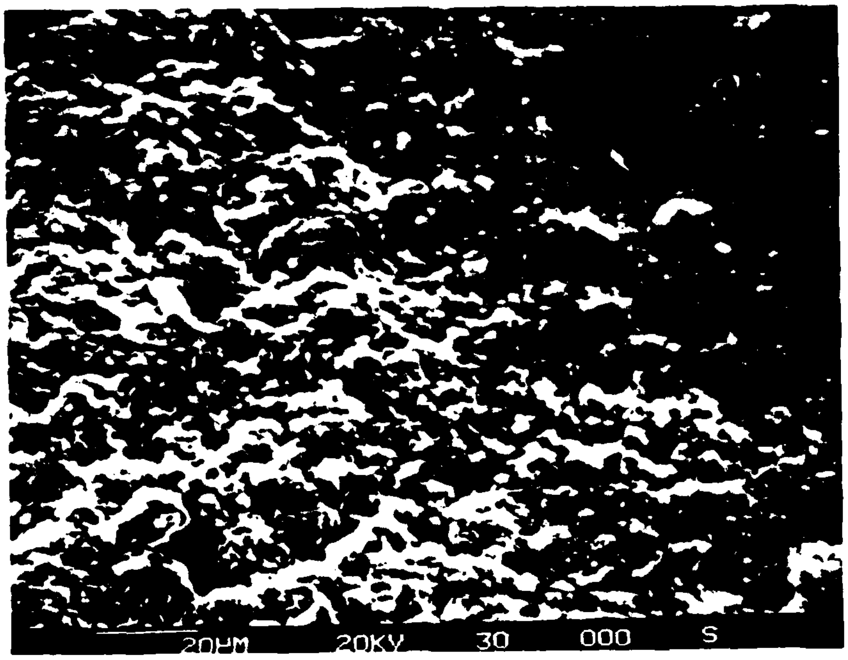

FIG. 14 Painted test panel immersed in Avtur. Water droplet added to left hand side of paint. Note similarities of paint under water droplet to Fig. 11.

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ABSTRACT

Failure of replacement coatings on the wing pivot fittings in integral wing fuel tanks of F111 aircraft has resulted in serious corrosion and pitting on critical sections of the fittings. Failed paint flakes from the fittings were characterised by adhesive detachment of the epoxy polyamide priming coat. Examination of fuel and moisture resistance of a range of possible coatings has been undertaken against those currently in use. The results suggest that coatings based on epoxy polyamide resins are sensitive to glycol ether compounds employed as fuel system icing inhibitors in aviation turbine fuels. A more resistant epoxy polyurethane paint coating has therefore been proposed for use on the inspection areas of the fittings. It is also recommended that respraying over existing coatings inside the wing fuel tanks and on the fittings away from the inspection areas, a practice that has led to a series of intercoat adhesion failures following overhaul, be discontinued.

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